JC20 Rec'd PCT/PTO 13 OCT 2005 PCT/EP2004/003697

WO 2004/092260

5

1

Novel stabilising system for halogenous polymers

The invention relates to stabilizer systems encompassing at least one perfluoroalkanesulphonate salt and at least one or more compounds from the groups consisting of the indoles, ureas, alkanolamines and aminouracils, which are suitable for stabilizing halogen-containing polymers.

- A halogen-containing polymer, such as PVC, may be stabilized by any of a large number of additives. Compounds of lead, of barium, and of cadmium are particularly well suited to this purpose, but are nowadays controversial for environmental reasons or
- because of their heavy metal content (cf. "Plastics Additives Handbook", H. Zweifel, Carl Hanser Verlag, 5th Edition, 2001, pp. 427-483, and "Kunststoff Handbuch PVC" [Plastics Handbook PVC], Volume 2/1, W. Becker and D. Braun, Carl Hanser Verlag, 2nd Edition,
- 1985, pp. 531-538; and Kirk-Othmer: "Encyclopedia of Chemical Technology", 4th Edition, 1994, Vol. 12, Heat Stabilizers, pp. 1071-1091).

There is therefore a continuing search for effective 25 stabilizers and stabilizer systems which are free from lead, barium and cadmium.

It has now been found that systems made from at least one or more compounds from the groups consisting of the indoles, ureas, alkanolamines and aminouracils and from at least one perfluoroalkanesulphonate salt, are particularly highly suitable for stabilizing chlorine-containing polymers, in particular PVC.

- 35 The invention accordingly provides stabilizer systems comprising at least
 - a) one perfluoroalkanesulphonate salt and

b) at least one or more indoles and/or ureas and/or alkanolamines and/or aminouracils

where the indoles have the general formula (I)

5

$$(R^4)_{m}$$
 R^3 (I)

where

m = 0, 1, 2 or 3;

 $R^3 = C_1-C_{18}-alkyl$, $C_2-C_{18}-alkenyl$, phenyl or

10

 C_7-C_{24} -alkylphenyl, C_7-C_{10} -phenylalkyl or C_1-C_4 -alkoxy; R^4 , R^5 = H, C_1-C_4 -alkyl, or C_1-C_4 -alkoxy;

where the ureas have the general formula (II)

$$\begin{array}{c|cccc}
R^{9} & & & & \\
N & & & & \\
N & & & & \\
R^{6} & & & & \\
R^{7} & & & &
\end{array}$$
 (II)

where

Y = O, S or NH;

 R^6 , R^7 , R^8 and R^9 , independently of one another, are H,

 C_1 - C_{18} -alkyl, where appropriate substituted with hydroxy groups and/or C_1 - C_4 -alkoxy groups, C_2 - C_{18} -alkenyl,

phenyl, where appropriate substituted with up to 3 hydroxy and/or C₁-C₄-alkyl/alkoxy groups, C₇-C₂₀-alkylphenyl or C₇-C₁₀-phenylalkyl and 2-substituents selected from

 $\text{C}_7\text{-}\text{C}_{10}\text{-}\text{phenylalkyl}$ and 2-substituents selected from R^6 to $\text{R}^9,$ where these may also form a ring,

and the urea used may also be a dimerized or trimerized urea, e.g. biuret or 1,3,5-tris(hydroxyalkyl) isocyanurate and possible reaction products of these,

5

where the alkanolamines have the formula (III)

$$R^{1} = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3} - O + H$$

$$N = N + (CHR_{a}^{3})_{y} - CHR_{b}^{3}$$

10 where x = 1, 2 or 3;y = 1, 2, 3, 4, 5 or 6;n = 1-10; R^1 and R^2 = independently of one another 15 Η, $C_1-C_{22}-alkyl$, $-[-(CHR^3_a)_V-CHR^3_b-O-]_n-H$, $-[-(CHR_{a}^{3})_{v}-CHR_{b}^{3}-O-]_{n}-CO-R_{d}^{4}$ C_2-C_{20} -alkenyl, 20 $C_2-C_{18}-acyl$, $C_4\text{-}C_8\text{-}\text{cycloalkyl}$, which may have OH substitution in the β -position, phenyl, C_7 - C_{10} -alkylphenyl or C_7 - C_{10} -phenylalkyl, 25 or if x = 1, R^1 and R^2 may also form, together with the N, a closed 4-10-membered ring of carbon atoms and, where appropriate, of up to 2 heteroatoms,

or if x = 2, R^1 may also be C_2 - C_{18} -alkylene which may have OH substitution at the two β -carbon atoms and/or may have interruption by one of more O atoms and/or by one or more NR^2 groups, or may be dihydroxy-substituted tetrahydrodicyclopentadienylene, dihydroxy-substituted ethylcyclohexanylene,

dihydroxy-substituted 4,4'-(bisphenol-A-dipropyl ether)ylene, isophoronylene, dimethylcyclohexanylene, dicyclohexylmethanylene or 3,3'-

dimethyldicyclohexylmethanylene, and if x = 3, R^1 may also be trihydroxy-substituted (tri-N-propyl isocyanurate)triyl;

 R_a^3 and R^3b = independently of one another, C_1-C_{22} -alkyl,

 C_2 - C_6 -alkenyl,

phenyl,

5

 C_6-C_{10} -alkylphenyl,

H or

 CH_2-X-R^5 ,

where X = 0, S, -O-CO- or -CO-O-;

and the aminouracils have the formula (IVa) or (IVb)

20

where in the case of (IVa) $\ensuremath{R^1}$ and $\ensuremath{R^2}$, independently of one another, are

Η,

unsubstituted or C_1 - C_4 -alkyl- C_1 - C_4 -alkoxy- and/or

hydroxy-substituted phenyl, or are phenyl- C_1 - C_4 -alkyl which is unsubstituted or has

 $C_1-C_4-alkyl$,

 C_1-C_4 -alkoxy and/or

hydroxy substitution

on the phenyl ring,

 C_3-C_6 -alkenyl,

 $C_5\text{-}C_8\text{-}\mathrm{cycloalkyl}$, or are $C_3\text{-}C_{10}\text{-}\mathrm{alkyl}$ interrupted by at least one oxygen atom,

or are CH2-CHOH-R3, $R^3 = H or$ $C_1-C_4-alkyl$, C2-C4-alkenyl, 5 C_4-C_8 -cycloalkyl, phenyl, C7-C10-alkylphenyl or C_7 - C_{10} -phenylalkyl, and in the case of N- or N'-monosubstituted aminouracils R^1 or R^2 is also $C_3\text{-}C_{22}\text{-}alkyl$, and in the 10 case of (IVb) $R^2 = H$ or the radicals C_1-C_4 -alkyl, C₂-C₄-alkenyl, or C₄-C₈-cycloalkyl, phenyl, $C_6-C_{10}-alkylphenyl, C_7-C_{10}-phenylalkyl, -CH_2-X-R^4$, where $R^4 = H$, a $C_1 - C_{10}$ -alkyl or 15 a C2-C4-alkenyl radical or C_4 - C_8 -cycloalkyl, where appropriate also containing an oxirane ring; or where appropriate substituted with from 1 to 3 C_1 - C_4 -alkyl radicals, or with a benzoyl radical or C_2 - C_{18} -acyl radical, and X = 0 or 20 S: $R^3 = R^2$ or R^4 ; C_2 - C_6 -alkyl substituted with at least 1-5 OH groups and/or interrupted by at least 1 to a maximum of 4 O atoms, or is CH_2 - $CH(OH)R^2$ for stabilizing chlorine-containing polymers. In addition to compounds of the formulae (I) to(III), 25 at least one compound of the formula (IVa) may also be present, where $R^1 = R^2 = C_1 - C_{22}$ -alkyl or oleyl, and these aminouracils may moreover have been replaced entirely or to some extent by a corresponding structurally isomeric cyanoacetylurea. Preferred 30 C_1 - C_{22} -alkyl is methyl, butyl, octyl, lauryl and stearyl. The corresponding cyanoacetylureas are N-methyl-, -butyl-, -octyl-, -lauryl- or -stearyl-N'-methyl-, -butyl-, -octyl-, -lauryl- or -stearylcyanoacetylurea. 35

The perfluoroalkanesulphonate salts of the formula $(R_fSO_3)_nM$ are known to the person skilled in the art.

The underlying acids, and also salts, are described in Kirk Othmer, Encyclopedia of Chemical Technology, 4th Ed., John Wiley & Sons, New York, Vol 11, pp 558-564 (1994).

5

10

15

Examples are those of the formula $(C_mF_{2m+1}SO_3)_nM$ where M is Li, Na, K, Mg, Ca, Sr, Ba, Sn, Zn, Al, La or Ce. The index n is correspondingly the valency of M: 1, 2 or 3. The perfluoroalkanesulphonate salts here may be used in various familiar supply forms; e.g. as a salt or solution in water or in an organic solvent, or absorbed onto a carrier material, such as PVC, Ca silicate, zeolites or hydrotalcites. Examples are perfluoroalkanesulphonate salts which have been converted to complexes or solutions using alcohols (polyols, cyclodextrins) or using ether alcohols or using ester alcohols or using crown ethers.

Trifuoromethanesulphonic acid ("triflic acid") and its 20 salts ("triflates") are reviewed in Chem. Rev. 77, 69-90 (1977), for example.

It is preferable to use sodium triflate or potassium triflate.

25

30

35

The invention also provides combinations of the stabilizer systems encompassing at least one perfluoroalkanesulphonate salt and at least one or more compounds from the groups consisting of the compounds of the general formula (I) or (II) or (III) or (IV) with at least one or more other conventional additives or stabilizers. Preference is given to polyols and/or disaccharide alcohols, glycidyl compounds, hydrotalcites, zeolites (alkali metal aluminosilicates and alkaline earth metal aluminosilicates), fillers, metal soaps, alkali metal and alkaline earth metal compounds, such as oxides and hydroxides, lubricants, plasticizers, phosphites, hydroxycarboxylates,

pigments, epoxidized fatty esters and other epoxy compounds, antioxidants, UV absorbers and light stabilizers, optical brighteners and blowing agents. Particular preference is given to epoxidized soya oils, alkaline earth metal or aluminium soaps and phosphites.

Particular preference is given to those components which are suitable for producing physiologically non-hazardous products.

10

5

Also included are the possible reaction products of the components used.

Examples of additional components of this type are
listed and explained at a later stage below (cf.
"Handbook of PVC Formulating" by E. J. Wickson, John
Wiley & Sons, New York, 1993 and Synoptic Document
No. 7, Scientific Committee for Food (SCF) - EU).

20 Polyols and disaccharide alcohols

Examples of possible compounds of this type are: glycerol, pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylolethane, bis(trimethylolpropane), polyvinyl alcohol,

25 bis(trimethylolethane), trimethylolpropane, sugars, sugar alcohols.

Of these, preference is given to pentaerythritol, trimethylolpropane, sorbitol and the disaccharide alcohols such as Malbit, lactitol and cellobiitol, and

30 also Palatinit.

It is also possible to use polyol syrups, such as sorbitol syrup, mannitol syrup and maltitol syrup. Examples of the amounts of the polyols used are from 0.01 to 20 parts by weight, advantageously from 0.1 to

20 parts by weight and in particular from 0.1 to 10 parts by weight, based on 100 parts by weight of PVC. Glycidyl compounds

These contain the glycidyl group $-CH - (CH_2)_{\stackrel{\circ}{R_1}} \xrightarrow{O}$,

bonded directly to carbon, oxygen, nitrogen or sulphur atoms, either where both of R_1 and R_3 are hydrogen, R_2 is hydrogen or methyl and n = 0 or where R_1 and R_3

together are $-CH_2-CH_2-$ or $-CH_2-CH_2-$, R_2 then being hydrogen and n being 0 or 1.

It is preferable to use glycidyl compounds having two functional groups. However, it is also possible in principle to use glycidyl compounds having one, three

10 or more functional groups.

Use is predominantly made of diglycidyl compounds having aromatic groups.

The amounts used of the terminal epoxy compounds are preferably at least 0.1 part, preferably from 0.1 to 50

parts by weight, advantageously from 1 to 30 parts by weight and in particular from 1 to 25 parts, based on 100 parts by weight of PVC.

Hydrotalcites

The chemical composition of these compounds is known to the skilled worker, e.g. from the patents DE 3 843 581, US 4,000,100, EP 0 062 813 and WO 93/20135.

Compounds from the hydrotalcite series may be described by the following general formula

25 $M^{2+}_{1-x}M^{3+}_{x}(OH)_{2} (A^{b-})_{x/b} \cdot d H_{2}O$, where

 ${\rm M}^{2+}$ = one or more of the metals selected from the group consisting of Mg, Ca, Sr, Zn and Sn

 M^{3+} = Al or B,

30 Aⁿ an anion of valency n, b is a number from 1-2,

0 < x < 0.5,

d is a number from 0-20.

Preference is given to compounds with

35 $A^n = OH^-$, ClO_4^- , HCO_3^- , CH_3COO^- , $C_6H_5COO^-$, $CO_3^{2^-}$, $(CHOHCOO)_2^{2^-}$, $(CH_2COO)_2^{2^-}$, $CH_3CHOHCOO^-$, HPO_3^- or $HPO_4^{2^-}$;

Examples of hydrotalcites are $\text{Al}_2\text{O}_3 \cdot 6\text{MgO} \cdot \text{CO}_2 \cdot 12\text{H}_2\text{O} \text{ (i), } \text{Mg}_{4.5}\text{Al}_2 \text{ (OH)}_{13} \cdot \text{CO}_3 \cdot 3.5\text{H}_2\text{O} \text{ (ii), } \\ 4\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 9\text{H}_2\text{O} \text{ (iii), } 4\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 6\text{H}_2\text{O}, \\ \text{ZnO} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 8-9\text{H}_2\text{O} \text{ and } \text{ZnO} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 5-6\text{H}_2\text{O}.$

Very particular preference is given to types (i), (ii) and (iii).

Zeolites (aluminosilicates of alkali metals and/or of alkaline earth metals)

- These may be described by the following general formula $M_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot wH_2O$, where n is the charge on the cation M;
 - M is an element of the first or second main group, such as Li, Na, K, Mg, Ca, Sr or Ba;
- 15 y : x is a number from 0.8 to 15, preferably from 0.8
 to 1.2; and
 w is a number from 0 to 300, preferably from 0.5 to 30.
 Examples of zeolites are sodium aluminosilicates of the
 formulae
- Na₁₂Al₁₂Si₁₂O₄₈ · 27 H₂O [zeolite A], Na₆Al₆Si₆O₂₄ · 2 NaX · 7.5 H₂O, X = OH, halogen, ClO₄ [sodalite]; Na₆Al₆Si₃₀O₇₂ · 24 H₂O; Na₈Al₈Si₄₀O₉₆ · 24 H₂O; Na₁₆Al₁₆Si₂₄O₈₀ · 16 H₂O; Na₁₆Al₁₆Si₃₂O₉₆ · 16 H₂O; Na₅₆Al₅₆Si₁₃₆O₃₈₄ · 250 H₂O [zeolite Y], Na₈₆Al₈₆Si₁₀₆O₃₈₄ . 264 H₂O [zeolite X];
- or the zeolites which can be prepared by partial or complete exchange of the Na atoms by Li atoms, K atoms, Mg atoms, Ca atoms, Sr atoms or Zn atoms, for example $(Na,K)_{10}Al_{10}Si_{22}O_{64} \cdot 20 \ H_2O \ ; \ Ca_{4.5}Na_3[(AlO_2)_{12}(SiO_2)_{12}] \cdot 30$ $H_2O; \ K_9Na_3[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27 \ H_2O.$
- Very particular preference is given to Na zeolite A and Na zeolite P.

The hydrotalcites and/or zeolites may be used in amounts of, for example, 0.1 to 20 parts by weight, expediently 0.1 to 10 parts by weight and in particular

0.1 to 5 parts by weight, based on 100 parts by weight of halogen-containing polymer.

Fillers

Fillers such as calcium carbonate, dolomite, wollastonite, magnesium oxide, magnesium hydroxide, silicates, china clay, talc, glass fibres, glass beads, wood flour, mica, metal oxides or metal hydroxides,

- carbon black, graphite, rock flour, heavy spar, glass fibres, talc, kaolin and chalk are used. Preference is given to chalk (HANDBOOK OF PVC FORMULATING, E. J. Wickson, John Wiley & Sons, Inc., 1993, pp. 393 449) and reinforcing agents (TASCHENBUCH der
- 10 Kunststoffadditive [Plastics Additives Handbook],
 R. Gächter & H. Müller, Carl Hanser, 1990, pp. 549 615).

The fillers may be used in amounts of preferably at least one part by weight, for example 5 to 200 parts by

weight, expediently 10 to 150 parts by weight and in particular from 15 to 100 parts by weight, based on 100 parts by weight of PVC.

Metal soaps

- Metal soaps are primarily metal carboxylates, preferably of relatively long-chain carboxylic acids. Well-known examples of these are stearates, oleates, palmitates, ricinolates, hydroxystearates, dihydroxystearates and laurates, and also oleates and salts of
- relatively short-chain aliphatic or aromatic carboxylic acids, such as acetic acid, propionic acid, butyric acid, valeric acid, hexanoic acid, sorbic acid, oxalic acid, malonic acid, maleic acid, anthranilic acid, succinic acid, glutaric acid, adipic acid, fumaric
- 30 acid, citric acid, benzoic acid, salicylic acid, phthalic acids, hemimellitic acid, trimellitic acid, pyromellitic acid.

Metals which should be mentioned are: Li, Na, K, Mg, Ca, Sr, Ba, Zn, Al, La, Ce and rare earth metals. Use

is frequently made of so-called synergistic mixtures, such as barium/zinc stabilizers, magnesium/zinc stabilizers or calcium/magnesium/zinc stabilizers. The metal soaps may

be used either alone or in mixtures. An overview of common metal soaps is found in Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A16 (1985), pp. 361 et seq.

The metal soaps or mixtures of these may be used in amounts of, for example, 0.001 to 10 parts by weight, expediently 0.01 to 8 parts by weight, particularly preferably 0.05 to 5 parts by weight, based on 100 parts by weight of PVC.

10

Alkali metal and alkaline earth metal compounds

For the purposes of the present invention, these are
mainly the carboxylates of the acids described above,
but also corresponding oxides or, respectively,

- hydroxides or carbonates. Mixtures of these with organic acids are also possible. Examples are LiOH, NaOH, KOH, CaO, Ca(OH)₂, MgO, Mg(OH)₂, Sr(OH)₂, Al(OH)₃, CaCO₃ and MgCO₃ (and also basic carbonates, such as magnesia alba and huntite), and also fatty-acid salts
- of Na and of K. In the case of alkaline earth carboxylates and Zn carboxylates it is also possible to use adducts of these with MO or M(OH)₂ (M = Ca, Mg, Sr or Zn), so-called "overbased" compounds. In addition to the stabilizers according to the invention it is
- 25 preferable to use alkali metal carboxylates, alkaline earth metal carboxylates and/or aluminium carboxylates.

Lubricants

Examples of possible lubricants are: fatty acids, fatty alcohols, montan wax, fatty acid esters, PE waxes, amide waxes, chloroparaffins, glycerol esters and alkaline earth metal soaps, and fatty ketones, and also the lubricants, or combinations of the lubricants, listed in EP 0 259 783. Stearic acid, stearic esters and calcium stearate are preferred.

Plasticizers

Examples of organic plasticizers are those from the following groups:

- A) Phthalates: examples of these plasticizers are dimethyl, diethyl, dibutyl, dihexyl, di-2-ethylhexyl, di-n-octyl, diisooctyl, diisononyl, diisodecyl, diisotridecyl, dicyclohexyl, dimethylcyclohexyl, dimethylglycol, dibutylgycol, benzyl butyl and diphenyl phthalate, and also mixtures of phthalates, such as
- 10 C₇-C₉- and C₉-C₁₁-alkyl phthalates composed of predominantly linear alcohols,

 C₆-C₁₀-n-alkyl phthalate and C₈-C₁₀-n-alkyl phthalates.

 Among these, preference is given to dibutyl, dihexyl, di-2-ethylhexyl, di-n-octyl, diisooctyl, diisononyl,
- diisodecyl, diisotridecyl and benzyl butyl phthalate, and also to the mixtures mentioned of alkyl phthalates. Particular preference is given to di-2-ethylhexyl, diisononyl and diisodecyl phthalate, also known by the common abbreviations DOP (dioctyl phthalate, di-2-
- 20 ethylhexyl phthalate), DINP (diisononyl phthalate), DIDP (diisodecyl phthalate).
 - B) Esters of aliphatic dicarboxylic acids, in particular esters of adipic, azelaic or sebacic acid: Examples of these plasticizers are di-2-ethylhexyl
- adipate, diisooctyl adipate (mixture), diisonoyl adipate (mixture), diisodecyl adipate (mixture), benzyl butyl adipate, benzyl octyl adipate, di-2-ethylhexyl azelate, di-2-ethylhexyl sebacate and diisodecyl sebacate (mixture). Preference is given to di-2-
- ethylhexyl adipate and diisooctyl adipate. C) Trimellitic esters, such as tri-2-ethylhexyl trimellitate, triisodecyl trimellitate (mixture), triisotridecyl trimellitate, triisooctyl trimellitate (mixture), and also tri- C_6 - C_8 -alkyl, tri- C_6 - C_{10} -alkyl,
- tri- C_7 - C_9 -alkyl and tri- C_9 - C_{11} -alkyl trimellitate. The last-mentioned trimellitates are formed by esterification of trimellitic acid with the corresponding alkanol mixtures. Preferred trimellitates

are tri-2-ethylhexyl trimellitate and the trimellitates mentioned obtained from alkanol mixtures. Common abbreviations are TOTM (trioctyl trimellitate, tri-2-ethylhexyl trimellitate), TIDTM (triisodecyl

- 5 trimellitate) and TITDTM (triisotridecyl trimellitate).
 - D) Epoxy plasticizers: these are primarily epoxidized unsaturated fatty acids, e.g. epoxidized soybean oil.
 - E) Polymeric plasticizers: a definition of these plasticizers and examples of the same are given in
- "Kunststoffadditive" [Plastics Additives], R. Gächter and H. Müller, Carl Hanser Verlag, 3rd Edition, 1989, Chapter 5.9.6, pp. 412-415, and in "PVC Technology", W. V. Titow, 4th Edition, Elsevier Publ., 1984, pp. 165-170. The commonest starting materials for preparing
- polyester plasticizers are: dicarboxylic acids, such as adipic, phthalic, azelaic or sebacic acid; diols, such as 1,2-propanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol and diethylene glycol.
 - F) Phosphoric esters: a definition of these esters is
- given in the abovementioned "Taschenbuch der Kunststoffadditive" ["Plastics Additives Handbook"], Chapter 5.9.5, pp. 408-412. Examples of these phosphoric esters are tributyl phosphate, tri-2-ethylbutyl phosphate, tri-2-ethylbutyl phosphate,
- 25 trichloroethyl phosphate, 2-ethylhexyl diphenyl phosphate, cresyl diphenyl phosphate, triphenyl phosphate, tricresyl phosphate and trixylenyl phosphate. Preference is given to tri-2-ethylhexyl phosphate and [®]Reofos 50 and 95 (Ciba Specialty
- 30 Chemicals).
 - G) Chlorinated hydrocarbons (paraffins)
 - H) Hydrocarbons
 - I) Monoesters, e.g. butyl oleate, phenoxyethyl oleate, tetrahydrofurfuryl oleate and alkylsulphonates.
- J) Glycol esters, e.g. diglycol benzoates.K) Citric esters, e.g. tributyl citrate and tributyl acetylcitrate, as described in WO 02/05206.

L) Perhydrophthalic, -isophthalic and -terephthalic esters, and also the perhydrogenated glycol and diglycol benzoates. Preference is given to diisononyl perhydrophthalate (**Hexamoll DINCH - BASF), as described in DE 19.756.913, DE 19.927,977, DE 19.927.978 and DE 19.927.979.

A definition of these plasticizers and examples of the same are given in "Kunststoffadditive" ["Plastics

- Additives"], R. Gächter/H. Müller, Carl Hanser Verlag, 3rd Ed., 1989, Chapter 5.9.6, pp. 412 415, and in "PVC Technology", W. V. Titow, 4th Ed., Elsevier Publ., 1984, pp. 165 170.
- Definitions and examples of plasticizers of groups G) to J) can be found in the following manuals:

 "Kunststoffadditive" ["Plastics Additives"], R. Gächter and H. Müller, Carl Hanser Verlag, 3rd Edition, 1989, Chapter 5.9.14.2, pp. 422-425, (group G), and Chapter
- 5.9.14.1, p. 422, (group H).
 "PVC Technology", W. V. Titow, 4th Edition, Elsevier
 Publ., 1984, Chapter 6.10.2, pp. 171-173, (group G),
 Chapter 6.10.5 p. 174, (group H,) Chapter 6.10.3, p.
 173, (group I) and Chapter 6.10.4, pp. 173-174 (group
 J).
- It is also possible to use mixtures of different plasticizers.

The plasticizers may be used in amounts of, for example, 5 to 20 parts by weight, expediently 10 to

20 parts by weight, based on 100 parts by weight of PVC. Rigid or semirigid PVC comprises preferably up to 10%, particularly preferably up to 5%, of plasticizer, or no plasticizer.

35 Pigments

5

Suitable substances are known to the skilled worker. Examples of inorganic pigments are TiO_2 , pigments based on zirconium oxide, $BaSO_4$, zinc oxide (zinc white) and

lithopones (zinc sulphide/barium sulphate), carbon black, carbon black-titanium dioxide mixtures, iron oxide pigments, Sb₂O₃, (Ti,Ba,Sb)O₂, Cr₂O₃, spinels, such as cobalt blue and cobalt green, Cd(S,Se), ultramarine blue. Examples of organic pigments are azo pigments, phthalocyanine pigments, quinacridone pigments, perylene pigments, diketopyrrolopyrrole pigments and anthraquinone pigments. TiO₂ in micronized form is also preferred. Mixtures of various pigments may also be used. A definition and further descriptions are found in the "Handbook of PVC Formulating", E.J. Wickson, John Wiley & Sons, New York, 1993.

Phosphites (triesters of phosphorous acid)

5

10

- Organic phosphites are known costabilizers for chlorine-containing polymers. Examples of these are trioctyl, tridecyl, tridodecyl, tritridecyl, tripentadecyl, trioleyl, tristearyl, triphenyl, tricresyl, tris(nonylphenyl), tris(2,4-tert-
- butylphenyl) and tricyclohexyl phosphite. Other suitable phosphites are various mixed aryl dialkyl or alkyl diarylphosphites, such as phenyl dioctyl, phenyl didecyl, phenyl didodecyl, phenyl ditridecyl, phenyl ditetradecyl, phenyl dipentadecyl,
- octyl diphenyl, decyl diphenyl, undecyl diphenyl, dodecyl diphenyl, tridecyl diphenyl, tetradecyl diphenyl, pentadecyl diphenyl, oleyl diphenyl, stearyl diphenyl and dodecyl bis(2,4-di-tert-butylphenyl) phosphite.
- Advantageous use may also be made of phosphites of various di- or polyols: e.g. tetraphenyldipropylene glycol diphosphite, polydipropylene glycol phenyl phosphite, tetramethylolcyclohexanol decyl diphosphite, tetramethylolcyclohexanol butoxyethoxyethyl
- diphosphite, tetramethylolcyclohexanol nonylphenyl diphosphite, bis(nonylphenyl) di(trimethylolpropane) diphosphite, bis(2-butoxyethyl) di(trimethylolpropane) diphosphite, tris(hydroxyethyl) isocyanurate hexadecyl

triphosphite, didecyl pentaerythrityl diphosphite, distearyl pentaerythrityl diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythrityl diphosphite, and also mixtures of these phosphites and aryl/alkyl phosphite

5 mixtures of empirical composition (H₁₉C₉-C₆H₄O)_{1.5}P(OC_{12,13}H_{25,27})_{1.5} or [C₈H₁₇-C₆H₄-O-]₂P[i-C₈H₁₇O], (H₁₉C₉-C₆H₄O)_{1.5}P(OC_{9,11}H_{19,23})_{1.5}.

Industrial examples are Naugard P, Mark CH 300, Mark CH 301, Mark CH 302, Mark CH 304 and Mark CH 55 (products of Crompton Corporation).

Examples of total amounts of the organic phosphites

Examples of total amounts of the organic phosphites used, or of mixtures thereof, are from 0.01 to 10 parts by weight, advantageously from 0.05 to 5, and in particular from 0.1 to 3 parts by weight, based on 100 parts by weight of PVC.

Metal hydroxycarboxylates

15

20

25

30

35

Metal hydroxycarboxylates may also be present, and the metal here may be an alkali metal or alkaline earth metal or aluminium. Preference is given to sodium, potassium, magnesium or calcium. The hydroxycarboxylic acid may be glycolic, lactic, malic, tartaric or citric acid, or salicylic or 4-hydroxybenzoic acid, or else glyceric acid, gluconic acid and saccharic acid (see patent specification GB 1,694,873).

Epoxidized fatty acid esters and other epoxy compounds
The stabilizer combination of the invention may
additionally and preferably comprise at least one
epoxidized fatty acid ester. Possible compounds here
are especially esters of fatty acids from natural
sources (fatty acid glycerides), such as soya oil or
rapeseed oil. However, it is also possible to use
synthetic products, such as epoxidized butyl oleate.
Use may also be made of epoxidized polybutadiene and
polyisoprene, if desired also in a partially
hydroxylated form, or of glycidyl acrylate and glycidyl
methacrylate as homo- or copolymer. These epoxy

compounds may also have been applied to a laminar compound; in this connection see also DE-A-4 031 818. Examples of total amounts of the epoxy compounds used are preferably at least 0.1 part by weight, for example from 0.1 to 50 parts by weight, advantageously from 1 to 30 and in particular from 1 to 25 parts by weight, based on 100 parts by weight of PVC.

Antioxidants

5

- Alkylated monophenols, e.g. 2,6-di-tert-butyl-4-methyl-phenol, alkylthiomethylphenols, e.g. 2,4-dioctylthiomethyl-6-tert-butylphenol, alkylated hydroquinones, e.g. 2,6-di-tert-butyl-4-methoxyphenol, hydroxylated thiodiphenyl ethers, e.g. 2,2'-thiobis(6-
- tert-butyl-4-methylphenol), alkylidenebisphenols, e.g. 2,2'-methylenebis(6-tert-butyl-4-methylphenol), benzyl compounds, e.g. 3,5,3',5'-tetratert-butyl-4,4'-dihydroxydibenzyl ether, hydroxybenzylated malonates, e.g. dioctadecyl 2,2-bis(3,5-di-tert-butyl-2-
- hydroxybenzyl) malonate, hydroxybenzyl aromatics, e.g. 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, triazine compounds, e.g. 2,4-bisoctylmercapto-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, phosphonates and
- phosphonites, e.g. dimethyl 2,5-di-tert-butyl-4hydroxybenzylphosphonate, acylaminophenols, e.g. 4hydroxylauranilide, esters of beta-(3,5-ditert-butyl-4hydroxyphenyl)propionic acid, beta-(5-tert-butyl-4hydroxy-3-methylphenyl)propionic acid, beta-(3,5-
- dicyclohexyl-4-hydroxyphenyl)propionic acid, esters of 3,5-ditert-butyl-4-hydroxyphenylacetic acid with monoor polyhydric alcohols, amides of beta-(3,5-ditert-butyl-4-hydroxyphenyl)propionic acid, such as, for example, N,N'-bis(3,5-ditert-butyl-4-hydroxyphenyl-
- propionyl) hexamethylenediamine, vitamin E (tocopherol) and derivatives. Mixtures of the antioxidants may also be used.

Industrial examples are Naugard 10, Naugard 76, Naugard BHT and Naugard 45 (products of Crompton Corporation). Examples of the amounts of the antioxidants used are from 0.01 to 10 parts by weight, advantageously from 0.1 to 10 parts by weight and in particular from 0.1 to 5 parts by weight, based on 100 parts by weight of PVC.

UV absorbers and light stabilizers

Examples of these are: 2-(2'-hydroxyphenyl)benzo-10 triazoles, such as 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-hydroxybenzophenones, esters of unsubstituted or substituted benzoic acids, such as 4tert-butylphenyl salicylate, phenyl salicylate, acrylates, nickel compounds, oxalamides, such as 4,4'-15 dioctyloxyoxanilide, 2,2'-dioctyloxy-5,5'-ditertbutyloxanilide, 2-(2-hydroxyphenyl)-1,3,5-triazines, such as 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4dimethylphenyl)-1,3,5-triazine, sterically hindered amines, such as bis(2,2,6,6-tetramethylpiperidin-4-yl) 20 sebacate, bis(2,2,6,6-tetramethylpiperidin-4-yl) succinate. Mixtures of the UV absorbers and/or light stabilizers may also be used.

25 Blowing agents

30

5

Examples of blowing agents are organic azo compounds and organic hydrazo compounds, tetrazoles, oxazines, isatoic anhydride, and also soda and sodium bicarbonate. Preference is given to azodicarbonamide and sodium bicarbonate and also mixtures of these.

Definitions for and examples of impact modifiers and processing aids, gelling agents, antistats, biocides, metal deactivators, optical brighteners, flame

35 retardants, antifogging agents and compatibilizers are given in "Kunststoffadditive" ["Plastics Additives"], R. Gächter/H. Müller, Carl Hanser Verlag, 3rd and 4th Ed., 1989 and 2001, and in "Handbook of Polyvinyl

Chloride Formulating", E. J. Wilson, J. Wiley & Sons, 1993, and also in "Plastics Additives", G. Pritchard, Chapman & Hall, London, 1st edition, 1998.

Impact modifiers are also described in detail in "Impact Modifiers for PVC", J. T. Lutz/D. L. Dunkelberger, John Wiley & Sons, 1992.

Use may be made of one or more additives and/or mixtures thereof may be used.

10

5

The invention also provides compositions which comprise a chlorine-containing polymer and a stabilizer system of the invention.

The invention also provides compositions which comprise a chlorine-containing polymer and a stabilizer system of the invention in addition to one or more other components from one of the groups exemplified by glycidyl compounds, phosphites, hydroxycarboxylates, hydrotalcites, zeolites, and alkali metal and alkaline earth metal compounds and epoxidized fatty esters.

The amounts of these compounds of the general formulae (I), (II), (III) and (IV) present for stabilization in these chlorine-containing polymer compositions are advantageously from 0.01 to 10 parts by weight, preferably from 0.05 to 5 parts by weight, in particular from 0.1 to 2 parts by weight based on 100 parts by weight of PVC.

30

35

25

Examples of the amount used of the perfluoroalkane-sulphonate compounds are from 0.001 to 5 parts by weight, advantageously from 0.01 to 3 parts by weight, particularly preferably from 0.01 to 2 parts by weight, based on 100 parts by weight of PVC.

The co-additives such as glycidyl compounds, phosphites, hydroxycarboxylates, hydrotalcites,

zeolites, and alkali metal and alkaline earth metal compounds and epoxidized fatty esters are used at from 0.01 to 15 parts by weight, preferably from 0.1 to 10 parts by weight, in particular from 2 to 3 parts by weight.

5

Examples of the chlorine-containing polymers to be stabilized are: polymers of vinyl chloride, of vinylidene chloride, vinyl resins whose structure contains vinyl chloride 10 units, such as copolymers of vinyl chloride and vinyl esters of aliphatic acids, in particular vinyl acetate, copolymers of vinyl chloride with esters of acrylic or methacrylic acid and with acrylonitrile, copolymers of 15 vinyl chloride with diene compounds and with unsaturated dicarboxylic acids or anhydrides of these, such as copolymers of vinyl chloride with diethyl maleate, diethyl fumarate or maleic anhydride, postchlorinated polymers and copolymers of vinyl 20 chloride, copolymers of vinyl chloride and vinylidene chloride with unsaturated aldehydes, ketones and others, such as acrolein, crotonaldehyde, vinyl methyl ketone, vinyl methyl ether, vinyl isobutyl ether and the like; polymers of vinylidene chloride and 25 copolymers of the same with vinyl chloride and with other polymerizable compounds; polymers of vinyl chloroacetate and of dichlorodivinyl ether; chlorinated polymers of vinyl acetate, chlorinated polymeric esters of acrylic acid and of alpha-substituted acrylic acid; 30 polymers of chlorinated styrenes, such as dichlorostyrene; chlorinated rubbers; chlorinated polymers of ethylene; polymers and postchlorinated polymers of chlorobutadiene and copolymers of these with vinyl chloride, chlorinated natural or synthetic rubbers, and also mixtures of the polymers mentioned 35 with themselves or with other polymerizable compounds. For the purposes of this invention, PVC includes

copolymers with polymerizable compounds, such as

acrylonitrile, vinyl acetate or ABS, where these may be suspension polymers, bulk polymers or else emulsion polymers. Preference is given to a PVC homopolymer, also in combination with polyacrylates.

5

10

15

20

25

Other possible polymers are graft polymers of PVC with EVA, ABS or MBS. Other preferred substrates are mixtures of the abovementioned homo- and copolymers, in particular vinyl chloride homopolymers, with other thermoplastic or/and elastomeric polymers, in particular blends with ABS, MBS, NBR, SAN, EVA, CPE, MBAS, PMA, PMMA, EPDM or with polylactones, in particular from the group consisting of ABS, NBR, NAR, SAN and EVA. The abbreviations used for the copolymers are familiar to the skilled worker and have the following meanings: ABS: acrylonitrile-butadienestyrene; SAN: styrene-acrylonitrile; NBR: acrylonitrile-butadiene; NAR: acrylonitrile-acrylate; EVA: ethylene-vinyl acetate. Other possible polymers are in particular styrene-acrylonitrile copolymers based on acrylate (ASA). A preferred component in this context is a polymer composition which comprises, as components (i) and (ii), a mixture of 25-75% by weight of PVC and 75-25% by weight of the copolymers mentioned. Components of particular importance are compositions made from (i) 100 parts by weight of PVC and (ii) 0-300 parts by weight of ABS and/or SANmodified ABS and 0-80 parts by weight of the copolymers

30

35

For the purposes of the present invention it is also possible to stabilize in particular recycled materials of chlorine-containing polymers, specifically the polymers described in more detail above, which have been degraded by processing, use or storage. Recycled material from PVC is particularly preferred.

NBR, NAR and/or EVA, but in particular EVA.

The compounds which may be used concomitantly according to the invention, and also the chlorine-containing polymers, are well known to the skilled worker and are described in detail in "Kunststoffadditive" ["Plastics Additives"], R. Gächter/H. Müller, Carl Hanser Verlag, 3rd and 4th Ed., 1989 and 2001; in DE 197 41 778 and in EP 967 245, which are incorporated herein by way of reference.

- 10 The stabilization according to the invention is particularly advantageous for rigid PVC formulations for transparent and non-transparent applications, as are common in pipes, profiles and sheets. For transparent applications, use is preferably made of 15 compounds of the formula (I), (II), (III) or (IVb) which have a melting point below about 190°C. The stabilization is also useful for semirigid and flexible formulations, and also in plastisols. The stabilization requires no heavy metal compounds (Sn stabilizers, Pb 20 stabilizers, Cd stabilizers, Zn stabilizers) and is particularly highly suitable for producing physiologically acceptable consumer products from PVC, including products for medical use.
- The stabilizer systems may advantageously be incorporated by the following methods: as emulsion or dispersion; as a dry mixture during the mixing of added components or polymer mixtures; by direct addition into the processing apparatus (e.g. calender, mixer, kneader, extruder or the like) or as a solution or melt or, respectively, as flakes or pellets in a dust-free form as one-pack.

The PVC stabilized according to the invention, which is also provided by the invention, may be prepared in a manner known per se, by using equipment known per se, such as the abovementioned processing apparatus, to mix the stabilizer system of the invention and, if desired,

other additives, with the PVC. The stabilizers here may be added individually or in a mixture, or else in the form of what are known as masterbatches.

5 The PVC stabilized as in the present invention may be brought into the desired shape in a known manner.

Examples of processes of this type are grinding, calendering, extruding, injection moulding and spinning, and also extrusion blowmoulding. The

10 stabilized PVC may also be processed to give foams.

A PVC stabilized according to the invention is, particularly suitable for example, for hollow articles (bottles), packaging films (thermoformed films), blown films, pipes, foams, heavy profiles (window frames), translucent-wall profiles, construction profiles, sidings, fittings, office sheeting and apparatus housings (computers, household devices).

Preference is given to rigid PVC foam moldings and PVC pipes, for example for drinking water or wastewater, pressure pipes, gas pipes, cable-duct pipes and cable-protection pipes, pipes for industrial pipelines, drainpipes, outflow pipes, gutter pipes and drainage pipes.

particularly suitable for semirigid and flexible formulations, in particular in the form of flexible formulations for wire sheathing, cable insulation, flooring, wallpapers, motor vehicle components,

30 flexible films, injection mouldings or hoses, these being particularly preferred. The inventive PVC in the form of semirigid formulations is particularly suitable for decorative films, foams, agricultural films, hoses, sealing profiles and office films. Examples of the use of the inventive PVC as plastisol are synthetic leather, flooring, textile coatings, wallpapers, coilcoating materials and underbody protection for motor

The PVC stabilized according to the invention is also

25

vehicles.

For more detail in this connection see "Kunststoffhandbuch PVC" ["Plastics Handbook PVC"], Vol. 2/2, W. Becker/H. Braun, 2nd Ed., 1985, Carl Hanser Verlag, pp. 1236 - 1277.

5

10

The examples below illustrate the invention but do not restrict the same. As in the remainder of the description, parts and percentages given are based on weight.

Examples

Table 1: Organic stabilizers

Stabilizer	Formula						
1	N H						
2	(NH-) ₂ C=S						
3	N-(CH ₂ -CH ₂ -OH) ₃						
4 a	H ₂ C=HC-H ₂ C N NH ₂						
4 b	H ₂ C=HC-CH ₂ -O-H ₂ C-HC-H ₂ C N N NH ₂ CH ₃						
5	O O O O O O O O O O						

Example 1: Static heat test

A dry mixture composed of

5

10

100.0 parts of	Evipol (trademark of EVC) SH 5730 -
	PVC, K value 57
5.0 parts of	Paraloid (trademark of Röhm & Haas)
	BTA 7805 = MBS (methyl methacrylate-
	butadiene-styrene) modifier
0.5 part of	Paraloid (trademark of Röhm & Haas)
	K 120 N = acrylate processing aid
0.5 part of	Paraloid (trademark of Röhm & Haas)
	K 175 N = acrylate processing aid
1.0 part of	Loxiol G 16 = partial fatty ester of
	glycerol (from Henkel)
0.3 part of	Wachs E = ester wax (Montane wax) (from
	BASF)
3.0 parts of	ESO = epoxidized soybean oil
0.1 part of	magnesium laurate
x parts of	sulphonate = 30% strength solution of
	Na trifluoromethanesulphonate in
	butyldiglycol

and 0.6 part of the stabilizers stated in table 1 were rolled on mixing rolls at 180°C for 5 minutes. The test strips of film, thickness 0.3 mm, were taken from the resultant milled sheet. The film specimens were heated in an oven (= Mathis Thermo-Takter) at 190°C. At 3-minute intervals the Yellowness Index (YI) was determined to ASTM D1925-70. The results are found in table 2. Low YI values mean good stabilization.

Table 2

i		Τ	T	\neg	 2	T	7	T		_		T		Τ	7	\neg	-	Т	7		T
	2	6	7		23.95	l c	• 1	39.93	66.33	92.39		103.67									
	S				37.88	30 63	0.00	72.04	114.20											_	
	4p	0 17	, + - >		7.35	8 14	۔ ا	• 1	13.98	17.38	0 70	• 1	32.64	40 06	٠١	54.39	64.95	1	91.14	97.82	118.78
	4p	,			7.16	7.81	0 17	. 1	17.08	18.74	10 70	17.	42.36	06 69		07.70	129.83				
	4a	0.05			8.66	9.77	12 29		10.01	20.01	25.49		32.90	42.20	בל בל	• !	75.42	124 91	• 1		
	4a	ì	סוו[בע 77		9.00	12.09	15.44	10 71	7 2	23.61	30.26	0	38.58	57.00	71 08	1	182.84				
	7	0.2		;	21.35	29.74	42.68	61 76		83.03	106.73										
	2	ı		1	33.84	50.59	87.68	146.02													
		0.1		16 76	72.70	18.20	24.07	40.12		55.32	70.99	שט		107.54	100.70						
		,		10 21	10.01	20.30	30.64	52.23	70 07	10.73	107.93										
	1	0.1		58 39		65.46	72.50	85.48	103 52	• 1									-		
1 1 1 2	scab.	x parts	Min	0		3	9	6	12	1	15	18		77	24	27		30	33		36

Comments

Table 2 clearly shows that addition of Na triflate to each type of stabilizer results in a significant improvement in initial colour, colourfastness and long-term stability.

Example 2: Static heat test

A dry mixture composed of

5

100.0 parts of	Evipol (trademark of EVC) SH 7020 -
	PVC, K value 70
47.0 parts of	Dioctyl phthalate
3.0 parts of	ESO = epoxidized soybean oil
0.3 part of	$Loxiol^{\otimes}$ G 71 S = pentaerythritol adipate
	complex ester - lubricant
0.1 part of	Calcium stearate
x parts of	sulphonate = 30% strength solution of
	Na trifluoromethanesulphonate

and 0.27 part of the stabilizers stated in table 1 were rolled on mixing rolls at 180°C for 5 minutes. The test strips of film, thickness 0.5 mm, were taken from the resultant milled sheet. The film specimens were heated in an oven (= Mathis Thermo-Takter) at 190°C. At 3-minute intervals the Yellowness Index (YI) was determined to ASTM D1925-70. The results are found in table 2. Where appropriate, 0.6 part of CH 300 = mixed aryl/alkyl phosphite from Crompton was added (cf. table 3) to the mixture. Low YI values mean good stabilization.

Table 3

	· · · · · · · · · · · · · · · · · · ·			
Stab.	3	3	3	3*
X part of	-	0.2	0.3	0.3
sulphonate				
Min		YI v	alue	
0	17.00	6.97	6.50	5.79
3	20.28	7.42	7.66	5.53
6	30.21	9.97	9.95	5.96
9	49.09	16.45	15.76	6.49
12	66.58	18.12	19.12	7.33
15	88.15	16.15	16.53	9.20
18	109.5	17.96	20.85	11.77
21		28.08	30.04	19.06
24		42.97	46.09	40.68
27		65.75	68.70	61.56
30		85.49	85.09	77.85
33		95.11	96.11	86.55
36		104.69	105.88	94.57
39				100.83

* + 0.6 part of CH 300 = mixed aryl/alkyl phosphite 5 from Crompton

Comments:

Table 3 shows that addition of Na triflate results in an improvement in thermal stabilizing action, which can be further improved via phosphite addition.

Example 3: Static heat test (TK 101 7790)

A dry mixture composed of

5

100.0 parts of	Evipol (trademark of EVC) SH 5730 -
	PVC, K value 57
5.0 parts of	Paraloid (trademark of Röhm & Haas)
	BTA 7805 = MBS (methyl methacrylate-
	butadiene-styrene) modifier
0.5 part of	Paraloid (trademark of Röhm & Haas)
	K 120 N = acrylate processing aid
0.5 part of	Paraloid (trademark of Röhm & Haas)
	K 175 N = acrylate processing aid
1.0 part of	Loxiol G 16 = partial fatty ester of
	glycerol (from Henkel)
0.3 part of	Wachs E = ester wax (Montane wax) (from
	BASF)
3.0 parts of	ESO = epoxidized soybean oil
x parts of	sulphonate = 30% strength solution of
	Na trifluoromethanesulphonate in
	butyldiglycol

and 0.3 part of the stabilizers stated in table 1 were rolled on mixing rolls at 180°C for 5 minutes. The test strips of film, thickness 0.3 mm, were taken from the resultant milled sheet. The film specimens were heated in an oven (= Mathis Thermo-Takter) at 190°C. At 3-minute intervals the Yellowness Index (YI) was determined to ASTM D1925-70. The results are found in table 4. Low YI values mean good stabilization.

Table 4

Stab.	3	3
X parts of	_	1.0
sulphonate		
Min	YI v	alue
0	45.9	14.12
3	54.1	18.18
6	77.45	21.99
9	111.6	28.13
12		38.20
15		53.15
18		73.60
21		91.47
24		105.39

Comments:

5 .

Addition of Na triflate gives a clear improvement in thermal stabilizing action as described in table 4.